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EVALUATION OF A RESERVE-PRIMARY ZINC/AIR BATTERY TO POWER THE A--ETC(U)
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RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
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DREO TECHNICAL NOTE NO. 77-17
DREO TN 77-17

EVALUATION OF A RESERVE-PRIMARY ZINC/AIR BATTERY TO POWER THE AN/TRN-30 BEACON

by

William A. Armstrong and Walter J. Moroz

PROJECT NO.
54-03-07

AUGUST 1977
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CAUTION

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ABSTRACT

Despite problems with leakage of electrolyte, disintegration of the separator material and air starvation at the cathodes, batteries gave four hours of discharge at 3A, while maintaining the battery voltage between 20-30V at temperatures between -40° and 49°C. Suggestions were made for improvements in the battery design.

RÉSUMÉ

Malgré des problems concernant la fuite de l'électrolyte, la disintégration du materiel utilisé comme séparateur et une manque d'oxygène aux cathodes, les batteries pouvaient supporter un debit, aux températures de -40° à 49°C, de 3A au cours de quatre heures en maintenant une tension de 20-30V.

INTRODUCTION

In February 1973 the Electrical Power Sources Division was approached by DEEM for advice on the selection of a primary battery to power the AN/TRN-30 non-directional beacon. The stated requirements were:

Power Output: 3A at 26-30 VDC normal
20-30 VDC abnormal

Duration of Operation: 4 hours continuous under environmental conditions from -40° to 49°C.

Weight: 10 lbs recommended maximum.

A review of the pertinent literature revealed that no available battery would meet the above requirements. At the time the United States Army proposed to use the BA-525, a mechanically rechargeable zinc/air battery, to meet this application. As this battery was activated by the addition of water, it could not be put into operation at temperatures below 0°C. It could, however, be activated at temperatures above the freezing point and subsequently discharged at lower temperatures. With this mode of operation, performance was unsatisfactory below -18°C. More recently a primary zinc/air, the BA-591, has been a strong candidate but neither it nor another possible candidate, a magnesium/manganese dioxide primary battery, are able to meet the Canadian Forces requirements at temperatures lower than -18°C.

After discussions with various battery manufacturers, DEEM was advised that the only advanced battery system which might be developed within a reasonable length of time and which would be capable of some useful performance at -40° was the reserve-primary zinc/air battery. It was estimated that such a battery weighing about 15 lbs would give 4 hrs of operation at -20°C and about 2 hrs at -40°. A contract demand was processed to develop and supply 50 prototype zinc/air batteries to the following specifications:

Electrical:

Temp °C	Voltage (VDC)	Current (Ampere)	Minimum Operating Period (Hr)
-40	20-30	3	2
-29	20-30	3	3
22	24-30	3	5
49	24-30	3	4

The battery must be capable of being activated within one minute at temperatures down to -40°C by personnel wearing gloves. Personnel shall not be physically exposed to the electrolyte. The length of time to reach the required optimum voltage and current levels at the specified temperatures below shall not be more than 5 minutes.

Physical:

a. Dimensions: Maximum physical dimensions permissible

Length	12.2"
Width	4.0"
Height	8.6"

b. Weight: Less than or equal to 15 lbs.

c. Shelf Life: In an unactivated state the battery must be capable of a minimum storage life of 2 years.

A contract was let to Unican Electrochemical Products Ltd. in February 1974 and 50 batteries were delivered to DREO in September 1975. As the primary goal of the contract was to demonstrate the feasibility of meeting the electrical performance specifications, the contractor was allowed to extend the length to 14 in and the weight to 18 lbs in order that readily available inexpensive materials might be used for the cell case.

Evaluation of the batteries at DREO according to the plan described in Appendix "A" was started in October 1975 and completed in July 1976.

DESCRIPTION OF THE BATTERY

As a detailed description of the battery is given in the final report by the contractor (1), the components will be described only briefly. Two batteries, one of which is unpainted so that the interior components can be seen, are shown in Figure 1.

ELECTROLYTE CONTAINER

The 33% potassium hydroxide electrolyte is contained in a plastic bag located in the upper compartment. With batteries 1 to 4 this bag was of low-density polyethylene but the remaining forty-six were equipped with a double bag. The inner bag was made of Melinex, a laminate of polypropylene

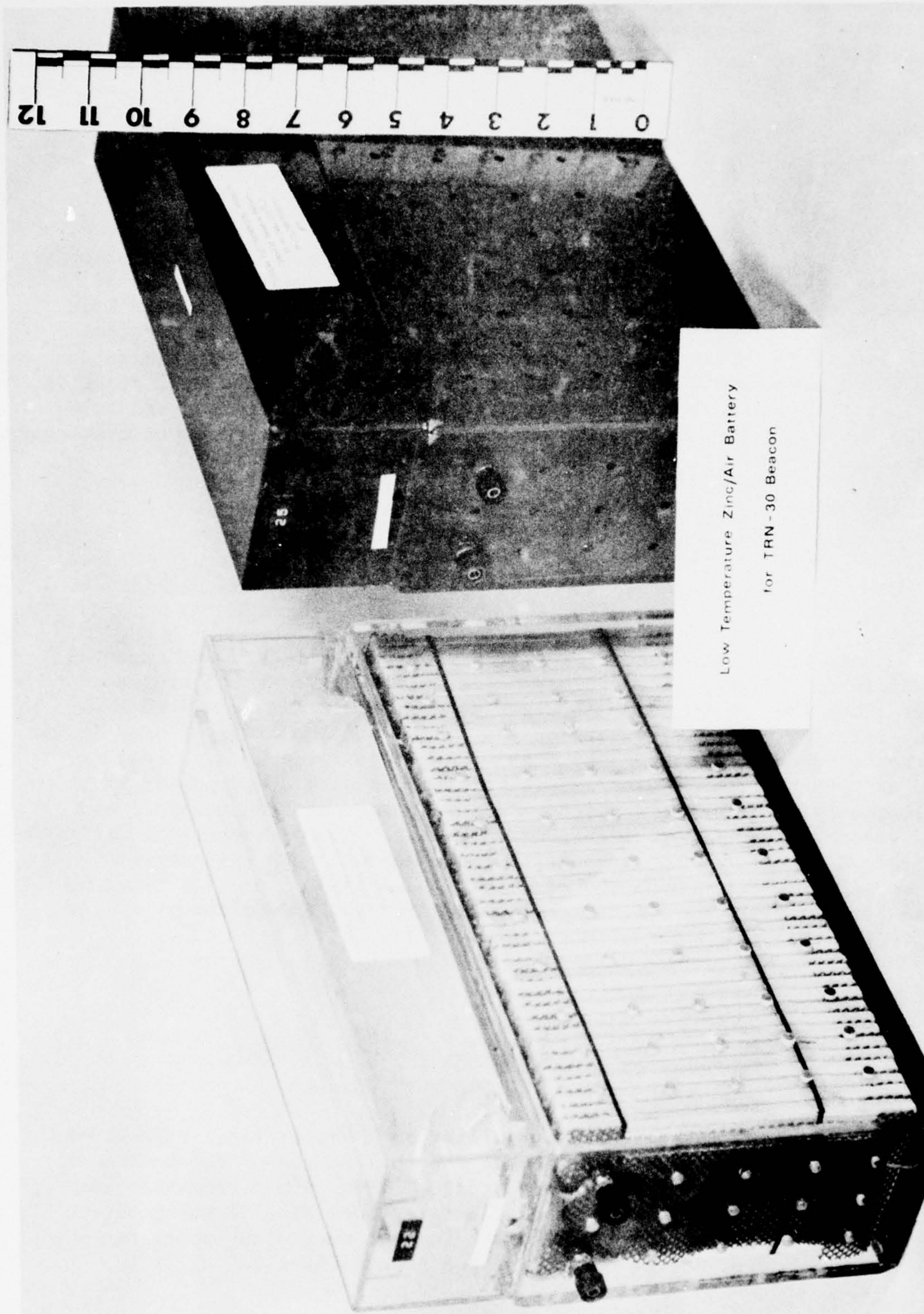

Fig. 1: Reserve-Primary Zinc/Air Battery

and polyester with the polypropylene facing inwards while the outer bag was of polyethylene. The bags were heat-sealed after the addition of the electrolyte.

CELL STACK

The cell stack, consisting of twenty-two modules connected electrically in series, is housed in the lower battery compartment the walls of which have rows of bored holes to permit access of air to the stack. Each module or "double bicell" is made up of two bicells connected in parallel and each bicell is separated from its neighbour by open-mesh plastic screen spacers which allow air to flow across the cathode faces. The cell stack is compressed to the size required to fit into the lower compartment and held firmly by two bands of rubber. The electrical leads are soldered to connectors which pass through the end wall of the cell stack compartment.

BICELL CONSTRUCTION

Each bicell consists of two 3.75 x 5.25 in air cathodes cemented to a 0.25 in cell frame. The cell frame is in two halves which are cemented together after the insertion of a 22 g zinc anode of dimensions 3.25 x 4.75 x 0.06 in. into the cell cavity between the cathodes. The catalyst used in the air cathodes is carbon impregnated with manganese dioxide by a process developed at DREO (2). This material is wet-proofed with a suspension of polytetrafluoroethylene (PTFE), applied to a semi-permeable PTFE membrane and pressed onto a expanded nickel current collector. A paper separator designed to electrically insulate the cathode from the anode covers the current collector and is glued around the edges of the cathode. The zinc anode is prepared by cold pressing a mixture of dendritic zinc and cellulose filler onto a copper grid. The porosity is greater than 75%.

ACTIVATION MECHANISM

The battery is activated by pulling on a metal ring. This causes two parallel knife blades to slide across the full length of the bottom of the electrolyte bag. The released electrolyte flows into a tray and from there into the top openings of each of the forty-four bicells which are cemented to the bottom of the tray. There is no common electrolyte path between bicells except during the activation process itself.

TEST APPARATUS

A Tenney Engineering Inc. environmental chamber, Model SST, was used to condition the batteries at the desired test temperature prior to discharge.

Room ambient discharges were normally carried out on an open laboratory bench. A 4 in. fan (Rotron) with a 100 ft^3/min capacity was used when required to augment air flow through the battery.

Continuous air feed (6 ft^3/h) to the batteries discharged in the chamber was maintained from a cylinder of compressed dry air with a flow control gauge (0-10 ft^3/h). For the battery test temperatures of -29° and -40°C the dry air from the cylinder was initially pre-cooled by passing it through copper coils immersed in a dry ice/methanol mixture contained in an insulated box. A heating bath was substituted for the cooling mixture when it was desired to pre-heat the dry air for the 49°C test temperature.

The batteries were discharged through a resistive load bank of 8 ± 0.1 ohm. The 8 ohm load was made up of six 50 ohm, 50 watt adjustable wire-wound resistors connected in parallel, with each resistor trimmed to 48 ohm.

Battery and cell voltage were monitored on a Digitec Datalogger, Model 1267, with a digital print-out. Simultaneous battery voltage and temperature traces were also recorded using a dual channel Hewlett-Packard 7100B strip chart recorder. A copper-constantin thermocouple enclosed in a protective glass envelope was inserted into the electrolyte of an inner cell module in order to measure changes in battery temperature during a discharge.

RESULTS

PRELIMINARY TESTING

A number of serious battery problems arose early in the test program which made it impossible to carry out the proposed evaluation plan (Appendix "A"). Ten batteries (Nos. 5-8, 13-16, 27 and 28) were returned to the contractor. These were reworked and discharged by the contractor in attempts to solve these problems. The battery faults and the proposed

solutions are discussed below.

ELECTROLYTE LEAKAGE

During activation about 200 ml of electrolyte leaked from the activation tray and the cell stack. A further 50-100 ml emerged while the battery was being discharged. Leakage was traced to three sources - the seal between the cell stack and the activation tray, the seam where the two halves of the cell frame had been glued together and the seal between the cathode and the cell frame. After removal of the cell stack from the battery case, the first two sources were easily accessible for re-sealing but the cathode-cell frame joints could not be reached without completely dismantling the cell stack.

Re-sealing the activation tray and cell frame joints reduced the leakage during activation and discharge to about 115 ml.

ELECTROLYTE CONTAINER SEALS

After a week of storage at high temperature and high humidity (32°C, 90%), electrolyte was observed leaking from the plastic bag of one of the batteries. Four of the ten batteries returned to the contractor were also found to be losing electrolyte. Leakage was attributed to poor heat-sealing of the plastic bag but there was also some evidence that the inner polyester coating was being attacked by the potassium hydroxide electrolyte. It was decided that a new type of electrolyte container was required.

INADEQUATE PERFORMANCE

Battery discharge performance at room temperature was erratic and considerably below the required 5 h. Two factors, one related to bicell design and the other to cell stack design were found to be responsible for the short discharge times.

During the development of the battery, difficulties were encountered in finding a separator which would wet when exposed to electrolyte at -40° (1). A filter paper met this requirement, performed satisfactorily in the cell stacks tested by the contractor and was used in all fifty of the batteries. However, it has since been found that this paper is of variable quality and some samples shrink and tear when exposed to electrolyte. This can result in cathode to anode shorts within the cell which reduce the battery voltage

and capacity. A double strength dynel bag open at the top was developed and appeared to be suitable for both high and low temperature operation. The opening at the top of the bag allowed electrolyte to flow on both sides of the separator and this promoted rapid wetting of the material even at very low temperatures. As the unsealing of cell frames would likely destroy both cathodes and anodes, new separators could not be introduced in a simple refurbishment of the batteries.

The second cause of poor battery performance at room temperature was air starvation of the cathodes. The minimum inter-cell spacing and hence the access of air to the cathodes was determined by the thickness of the open weave plastic spacer (0.045 in) but it was evident that there were differences in the distances between bicells as a result of non-uniform compression of the cell stack on insertion of the stack into the battery case. Actually three pieces of spacer were used between bicells but two occupied the space between the cathode face and the outer edge of the cell frame and only the middle spacer had tabs which extended between the two neighbouring frames (Figure 2). The spacers next to the cathode faces probably hindered the air flow.

REPAIR OF BATTERIES

None of the problems discussed above could be completely solved by simple repairs to existing batteries. However, ten more batteries (Nos. 3, 4, 29-36) were returned to the contractor for re-sealing of the activation trays and cell frame joints. To improve air circulation small wedges of of spacer material were inserted between bicells that were obviously poorly spaced, and two new rows of holes were drilled at the top and bottom of each lower battery compartment.

Before returning the cell stacks to their containers, the electrical resistance of each bicell was measured. Each battery had a number of shorted cells but these shorts were of an intermittent nature and were affected by a slight tapping or shaking of the cell stack. They were attributed to small amounts of fine zinc powder from the anode falling off and forming an intermittent conductive path between anode and cathode. Battery No. 33 had the greatest number of shorted cells (twelve) but when discharged at -40° behaved normally and met the specified run time.

The remaining nine batteries were returned to DREO.

EVALUATION OF BATTERIES

A Revised Evaluation Plan (Appendix "B") was drawn up, based on the information obtained from the preliminary tests and taking into account the reduced number of batteries. The results of the tests carried out as described in Appendix "B" are recorded below.

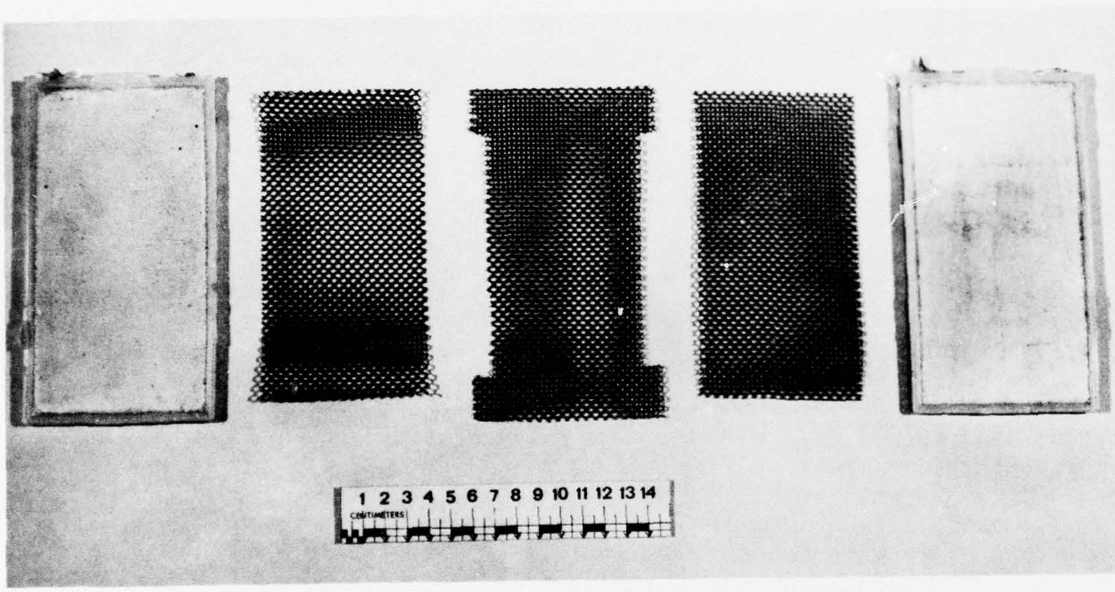

Fig. 2: Bicells and Screen Spacers

PHYSICAL INSPECTION

All forty batteries which originally arrived at DREO were undamaged and showed no evidence of electrolyte leakage. As there were only minor differences in recorded dimensions, only the measurements of the nine batteries re-sealed by the contractor are recorded in Table I.

TABLE I

Physical Condition and Dimensions of Batteries

Battery No.	Physical Damage	Electrolyte Leakage	Dimensions (in) w	h	l*	Weight** (lbs)
3	No	No	4.1	10.1	14.2	16.6
4	No	No	4.0	10.0	14.1	16.6
29	No	No	4.1	10.0	14.1	16.6
30	No	No	4.0	10.0	14.1	16.5
31	No	No	4.0	10.0	14.2	16.6
32	No	Yes	4.0	10.1	14.2	16.6
34	No	No	4.0	10.1	14.1	16.6
35	No	Yes	4.1	10.0	14.2	16.8
36	No	No	4.0	10.0	14.1	16.5

* Does not include protruding electrical connectors and activation ring.

** Includes outer plastic wrap.

COMMENTS

1. Batteries 32 and 35 were rendered unserviceable as a result of electrolyte entering the cell stack.

2. All batteries were 0.1 - 0.2 in. longer than the revised maximum permissible length of 14.0 in. and exceeded the specified height by 1.4 - 1.5 in.

3. All battery weights were in the range 16.5 - 16.8 lbs, well below the 18 lb revised maximum permissible.

EFFECT OF AIR CIRCULATION ON DISCHARGE TIME

In all discharges the time required to operate the activation mechanism was less than 2 sec, the time to attain an open circuit voltage (OCV) of 24V was about 4 sec and the battery voltage remained above 20V on application of the load.

Test (a): The results of the four batteries discharged in an "as received" condition are shown graphically in Figures 3-6. Discharge times ranged from 0 to 0.5 h to a 24V cut-off.

Test (b): Removal of the side panels of the lower battery compartment increased the length of discharge to 1.0 h to a 24V cut-off or 4.4 h to a 20V cut-off as illustrated in Figure 7.

Test (c): Initiation of the circulation fan when the battery voltage reached 20V after 1.1 h of discharge raised the voltage to about 26V and permitted a further 2.6 h of run time to 24V to be obtained (Figure 8).

Test (d): The longest discharge (4.0 h to 24V, 5.0 h to 20V) was obtained with the chamber door open and the fan in operation throughout the discharge (Figure 9).

COMMENTS

The results of the tests described in Section II of Appendix "B" indicate:

1. Despite the insertion of wedges between bicells the length of discharge during normal operation at ambient temperature is limited by the insufficient amount of air reaching the air cathode.

2. Extra holes in the cell case do not sufficiently increase convective air circulation. Even a battery with the case walls removed did not meet the discharge specification.

3. The battery discharged with forced air circulation gave the longest discharge time but did not meet the specified 5 h of operation to a 24V cut-off.

4. The degree of air circulation also affected the internal battery temperature. The highest temperature recorded during a discharge under condition Test (a) was 79°, under Test (b) 60°, Test (c) 31° and Test (d) 35°C.

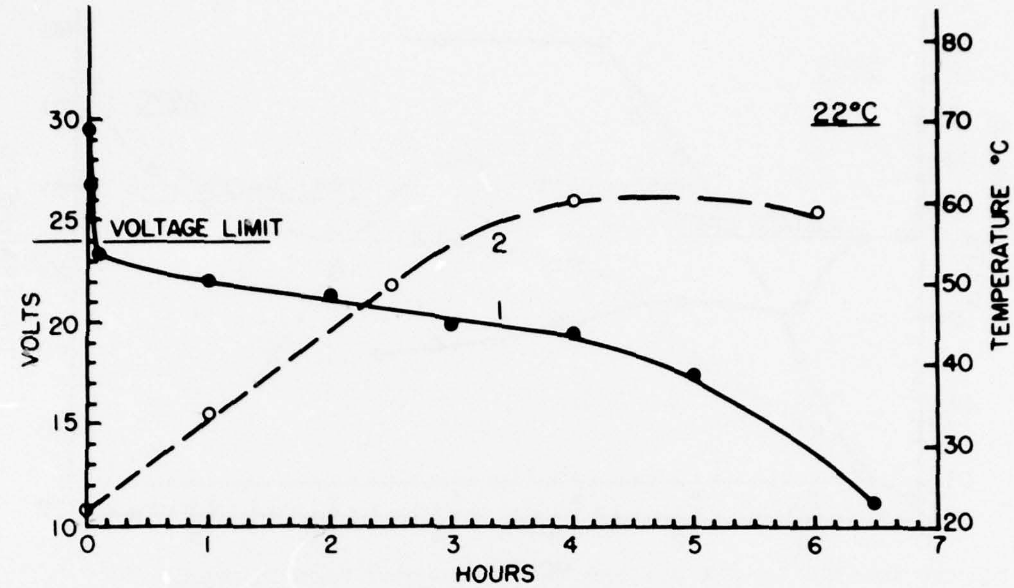

Fig. 3: Discharge at Room Temperature Without Forced Air Circulation of Battery No. 11.

1. Voltage 2. Temperature

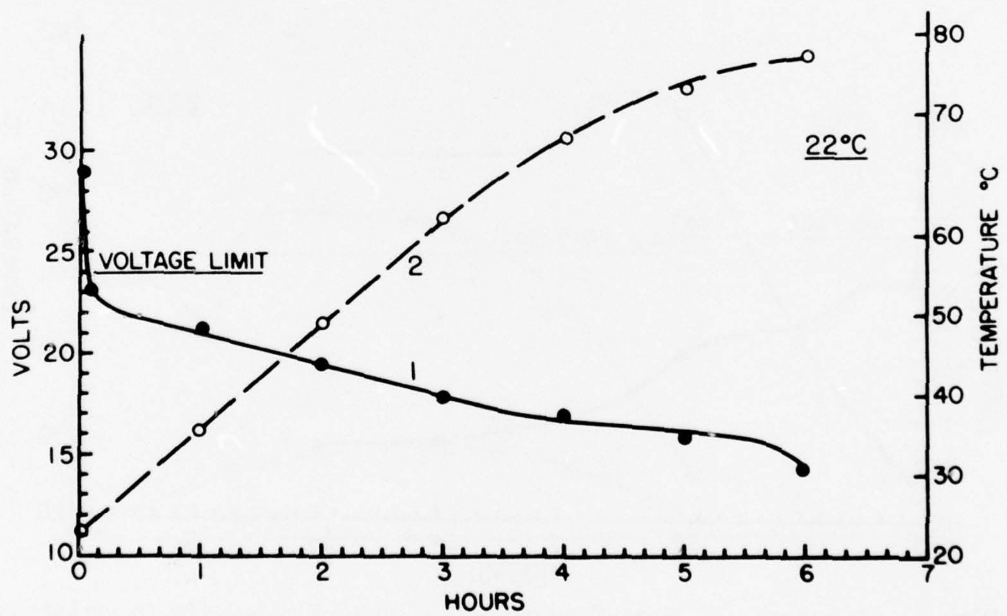

Fig. 4: Discharge at Room Temperature Without Forced Air Circulation of Battery No. 1.

1. Voltage 2. Temperature

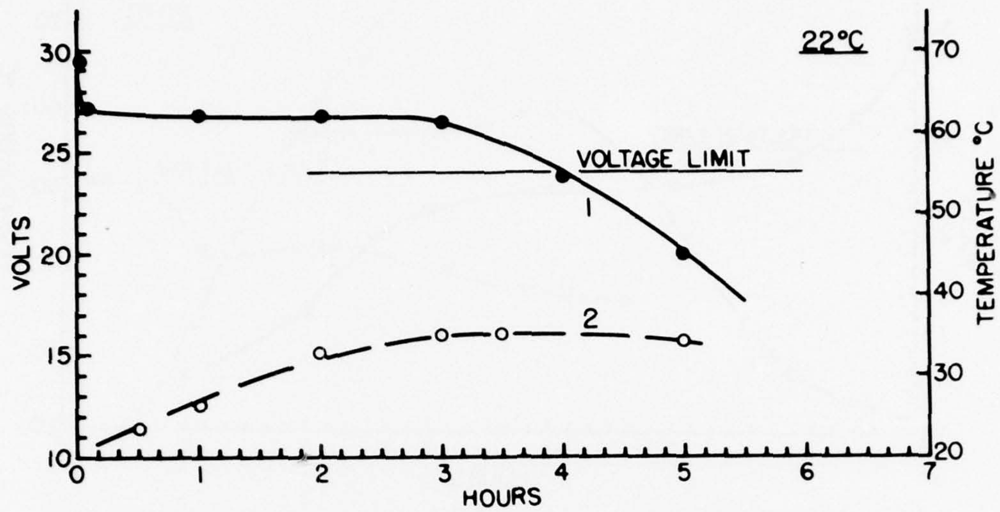

Fig. 9: Discharge at Room Temperature With Forced Air Circulation of Battery No. 48.

1. *Voltage* 2. *Temperature*

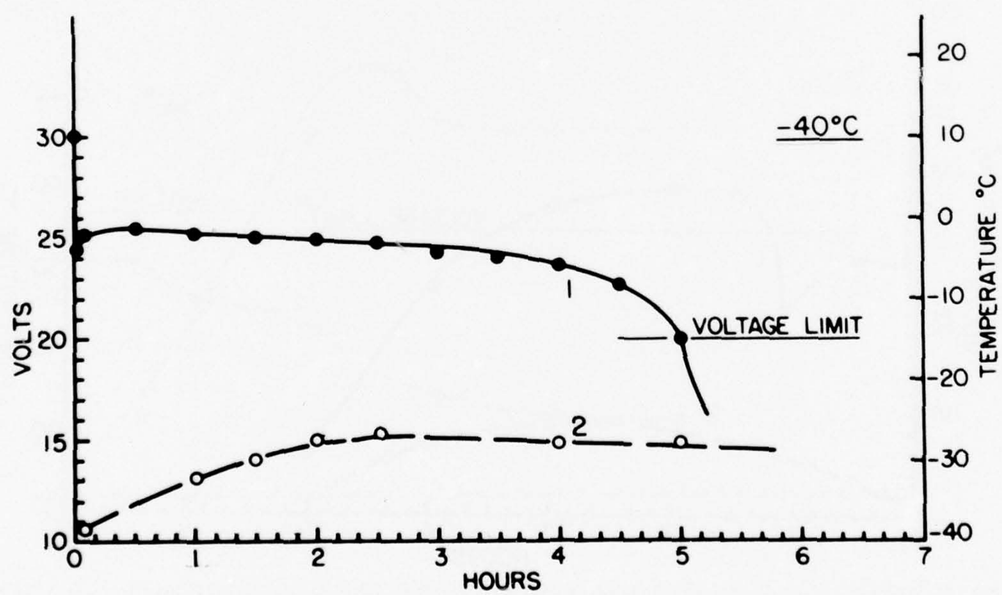

Fig. 10: Discharge at -40°C of Battery No. 42.

1. *Voltage* 2. *Temperature*

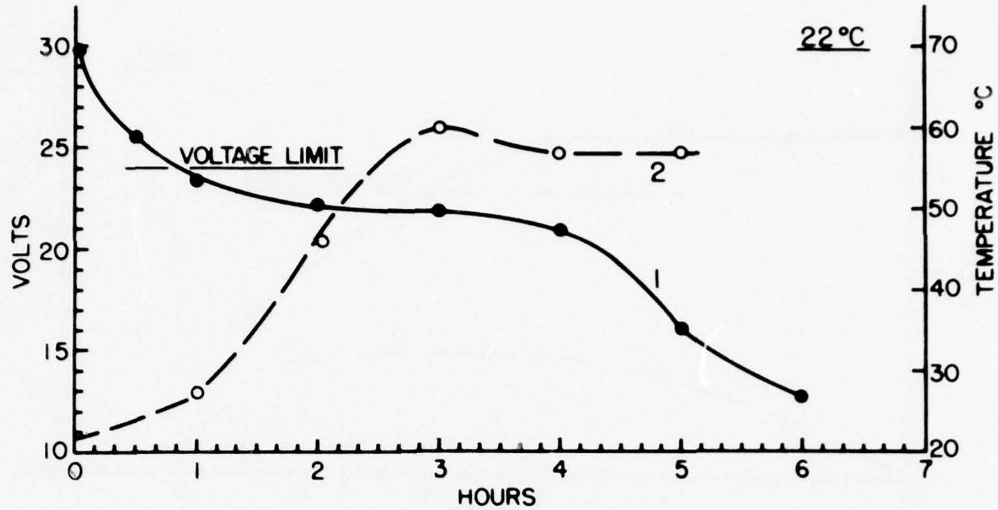

Fig. 7: Discharge at Room Temperature of Battery No. 46 Without Forced Air Circulation but with Lower Case Side Panels Removed.

1. Voltage 2. Temperature

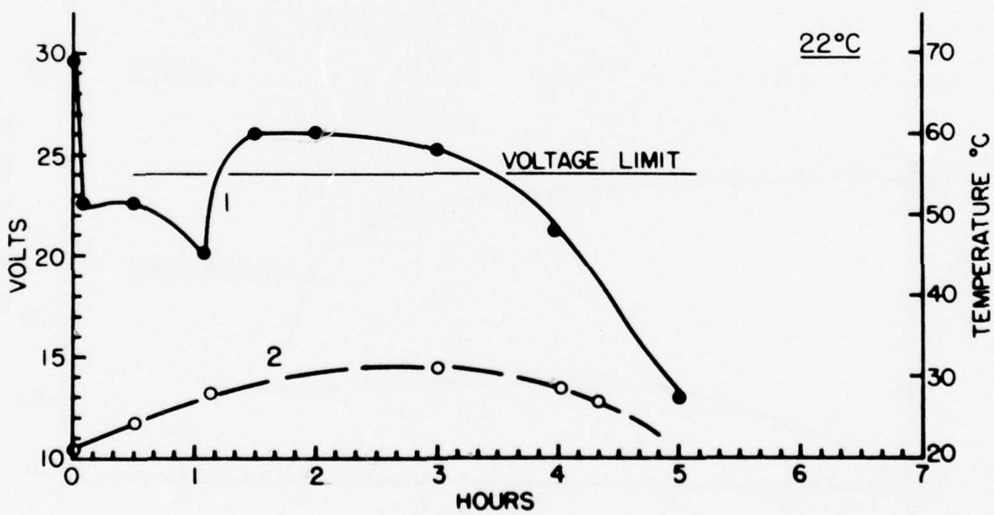

Fig. 8: Discharge at Room Temperature of Battery No. 4 With Forced Air Circulation Started When Battery Voltage Decreased to 20V.

1. Voltage 2. Temperature

CONTINUOUS ELECTRICAL DISCHARGE TESTS

The results of discharge Tests III(a) - III(d) (Appendix "B") are recorded in Figures 10-16 and summarized in Table II. It was demonstrated in the previous section that the specified 5 hours of operation to a 24V cut-off at 22°C could not be attained. For this reason and because of the small number of batteries available, no further discharges into the 8.0 ohm load were done at room temperature. Instead battery No. 36 was discharged at a constant current of 3.0A impressed by a power supply. This discharge was carried out on a bench with a small fan providing air circulation.

TABLE II

Results of Continuous Electrical Discharge Tests

Temperature °C	Battery No.	Time to Reach 24V OCV sec	Discharge Time to Specified Voltage* h	Maximum Electrolyte Temperature °C
-40	42	40	5.0	-28
	44	66	4.3	-30
-29	43	27	4.4	-17.5
	45	28	4.7	-24.5
22	36**	4	4.6	31
49	47	2	4.6	62
	49	2	5.7	56

* 20V cut-off for discharges at -40° and -29°, 24V for discharges at 22° and 49°.

** Discharged at a constant current of 3.0A impressed by a power supply and with a fan providing air circulation through the cell stack.

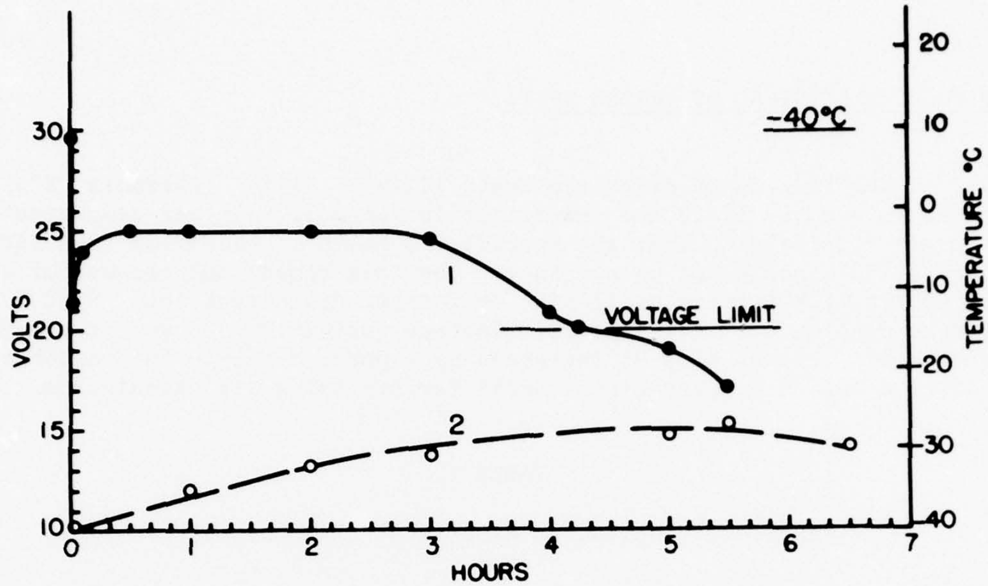

Fig. 11: Discharge at -40°C of Battery No. 44.
1. Voltage 2. Temperature

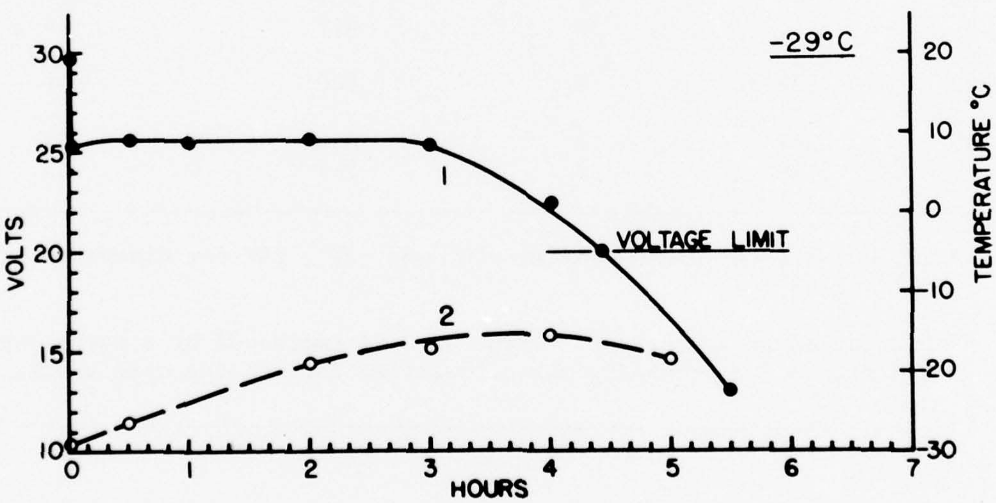

Fig. 12: Discharge at -29°C of Battery No. 43.
1. Voltage 2. Temperature

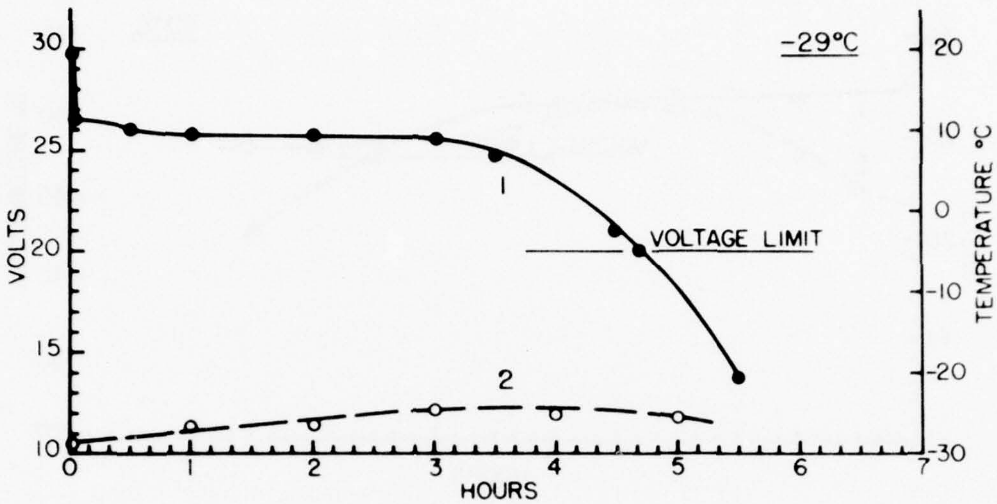

Fig. 13: Discharge at -29°C of Battery No. 45.
1. Voltage 2. Temperature

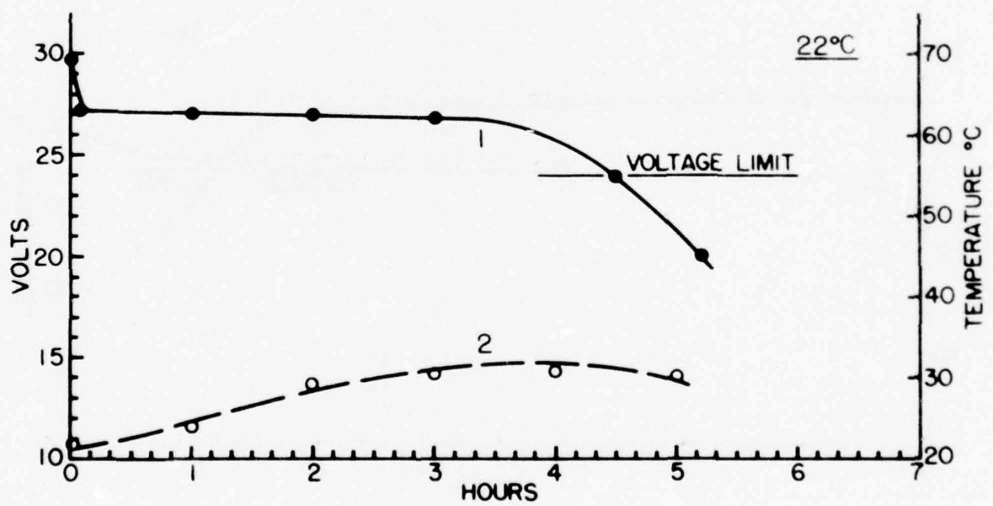

Fig. 14: Discharge at 22°C and a Constant Current of 3.0A of Battery No. 36.
1. Voltage 2. Temperature

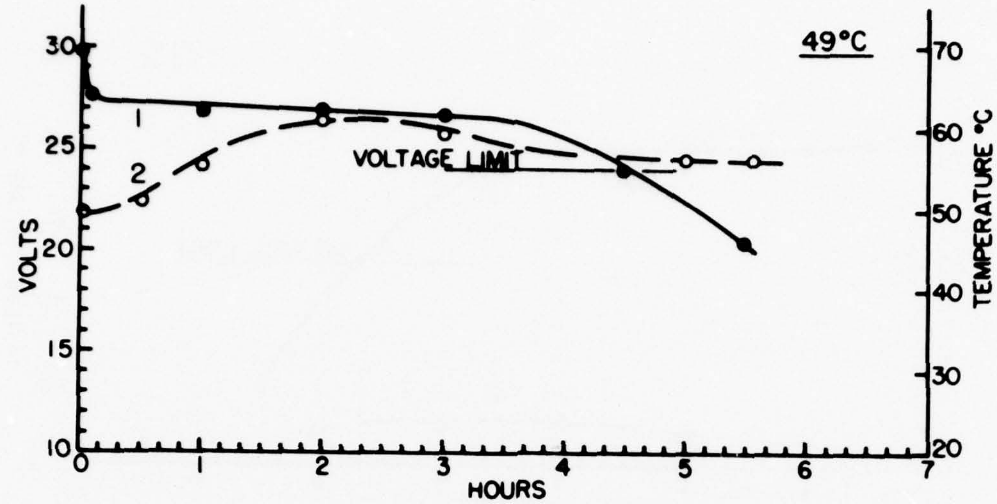

Fig. 15: Discharge at 49°C of Battery No. 47.
1. Voltage 2. Temperature

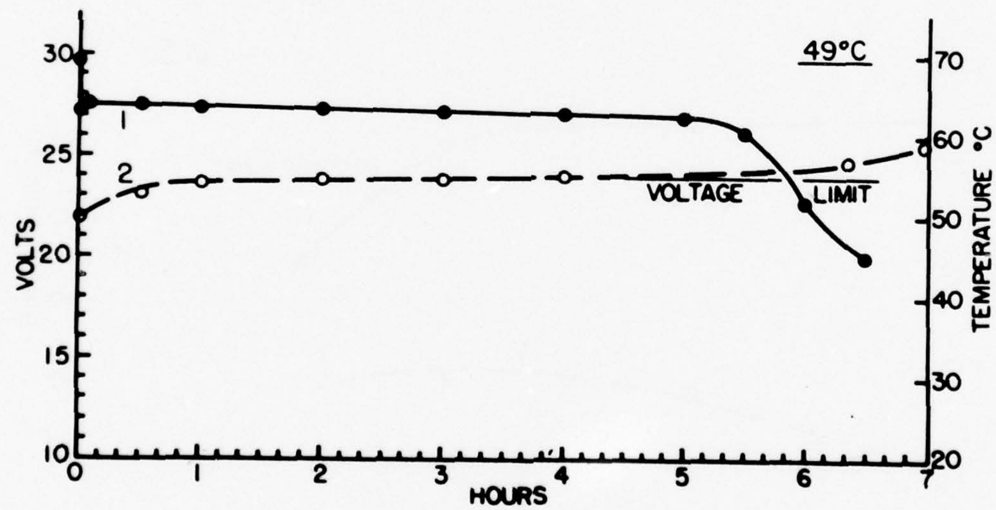

Fig. 16: Discharge at 49°C of Battery No. 49.
1. Voltage 2. Temperature

COMMENTS

1. All batteries met the specified activation requirements. Batteries were activated without difficulty in less than 2 sec at all temperatures. The length of time to reach acceptable voltage and current levels was much less than the specified maximum of 5 min.

2. The specified requirements for electrical performance were met at -40°, -29° and 49°. The battery force-discharged with an impressed current of 3.0A gave 4.6 h of service, 0.4 h short of the specification.

3. Problems of air starvation at the cathode were not encountered with batteries discharged in the environmental chamber because the operation of the chamber fan caused sufficient air to circulate through the cell stack.

4. The internal temperature of each of the batteries as measured in the electrolyte increased by approximately 10°C during discharge.

UNACTIVATED STORAGE

Test (a): Batteries Nos. 10, 11 and 12 were placed in a chamber at 32°C and 90% relative humidity. No. 11 was found to be leaking electrolyte after 7 days and No. 10 after 23 days. The test was stopped and the remaining battery removed.

Test (b): Battery No. 9 was stored at 71°C. Electrolyte leakage was noted after 1 week and dry KOH deposits were observed after 2 weeks as shown in Figure 17. The battery was examined after 30 days. Only about 900 ml of the original 1300 ml of electrolyte remained in the bag and the battery was declared inoperable.

Test (c): The results of the discharges performed after room temperature storage are recorded in Table III. Of the eight batteries stored, two were rendered inactive by leakage of electrolyte into the cell stack. After about 150 days it was noted that electrolyte had entered the space between the inner and outer bags of several other batteries. At that time all electrolyte bags were removed from the batteries and stored separately. This required removal of the outer plastic wrap from the batteries which were then stored unprotected from the humidity in the atmosphere. From results recorded by the contractor of the effects on zinc samples of storage at various temperatures and humidities (1), it could be predicted that unprotected storage would adversely affect battery performance, particularly at low temperatures. Therefore the discharge at -40° after 180 days, as well as the storage tests beyond 270 days were omitted.

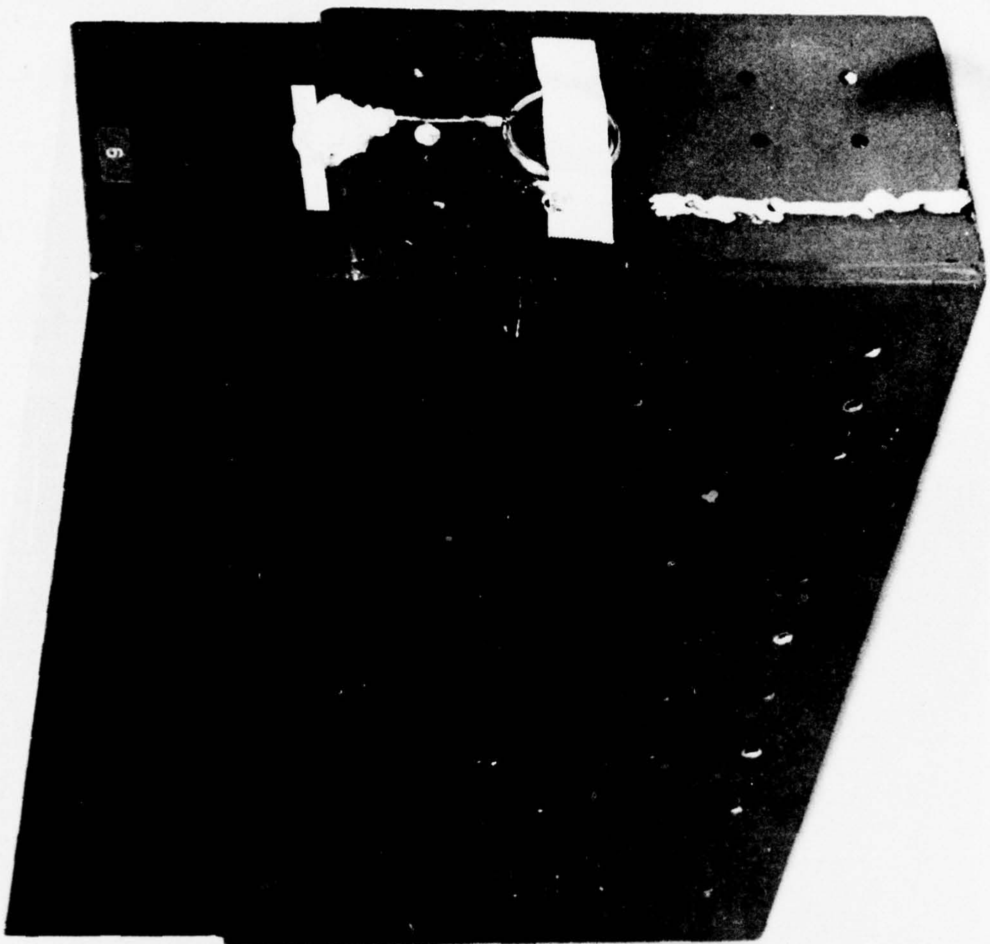

Fig. 17: Battery After Storage at 71°C.

TABLE III

Discharge of Batteries After Storage at Room Temperature

Length of Storage days	Battery No.	Discharge Temperature °C	Discharge Time to Specified Voltage* h	Maximum Electrolyte Temperature °C
90	18	22	3.6	41
	17	-40	1.8	-32
180	23	22	3.8	31
270	25	22	2.7	25
	24	-40	1.4	-36

* 20V cut-off for discharges at -40°, 24V for discharges at 22°C

COMMENTS

1. None of the stored batteries met the electrical specifications.

2. Leakage from the electrolyte bag was the cause of failure of batteries at 32° and 71°C.

3. Oxidation of zinc in batteries stored without a protective plastic wrap was the most likely cause of failure of batteries stored at room temperature.

ACTIVATED STORAGE

The results of discharges made following activated storage of Batteries 29 and 30 are shown in Figures 18 and 19. Four hours after being activated, Battery No. 29 was discharged 1.0 h to the 24V cut-off. Seven hours after activation, the OCV of Battery No. 30 was well below the 24V value and no discharge on load was possible.

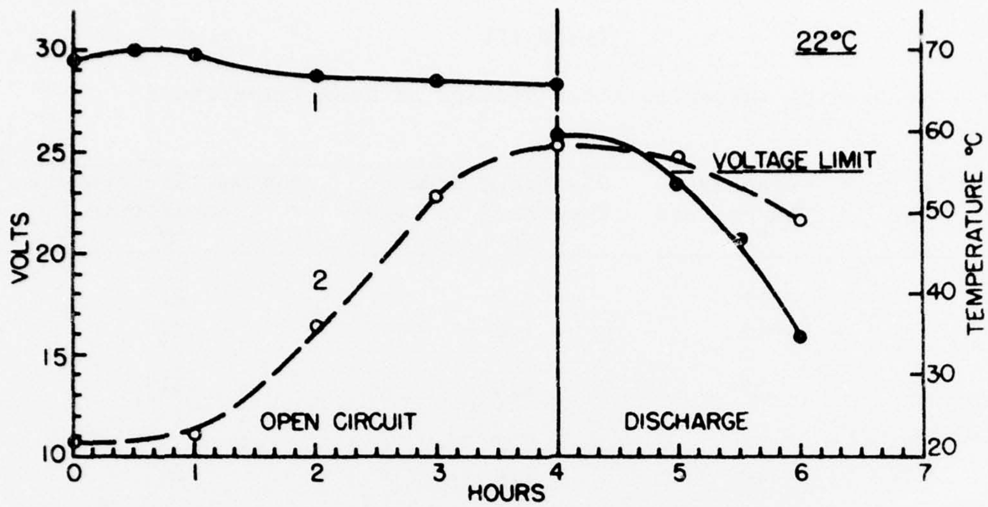

Fig. 18: Discharge After 4 h Activated Stand at Room Temperature of Battery No. 29.

1. Voltage 2. Temperature

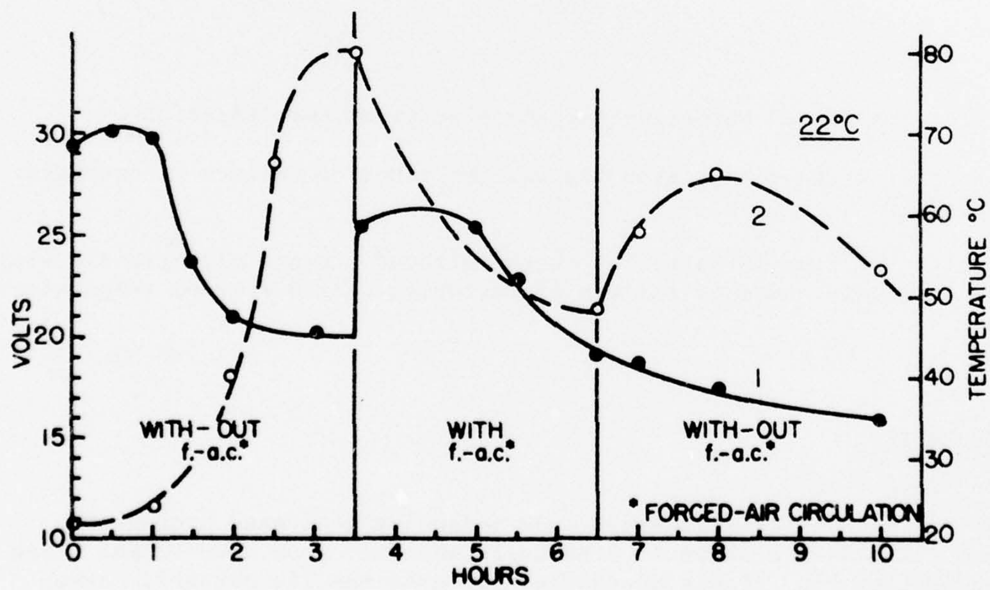

Fig. 19: Behaviour of Battery No. 30 During 24 h Activated Stand.

1. Voltage 2. Temperature

COMMENTS

1. Battery performance deteriorated to an unacceptable level during four hours stand after addition of electrolyte.

2. The increase in battery temperature during stand and the affect of air circulation on the OCV (Figures 18 and 19) indicate that the batteries were self-discharging at a rapid rate.

DISCHARGED STORAGE

No evidence of cell module distortion, damage to battery case or further leakage of electrolyte was found with any stored discharged battery.

EFFECT OF INDIVIDUAL CELL MODULE PERFORMANCE ON BATTERY PERFORMANCE

The individual cell voltages of Battery No. 34, one of those re-sealed by the contractor, are listed in Table IV while the electrode potentials with respect to a mercury/mercuric oxide reference electrode of cell 13 are plotted in Figure 20. Plots of total battery voltage and electrolyte temperature are given in Figure 21.

Periodically during the discharge, electrolyte that had leaked out was returned to cells which showed a low liquid level. About 210 ml were re-cycled in this way. It was noted that only cell module 13 did not lose electrolyte. Cell modules 3, 4, 5, 7, 14, 15, 17, 18 and 19 leaked only from one bicell while the remaining cells leaked from both. On addition of electrolyte to a cell, the cell voltage increased by about 5 mV but soon decayed to the previous level as leakage continued.

From Figure 20 it can be seen that potentials of both the zinc and air electrodes of cell 13 changed very little after the first hour of discharge. Both electrodes behaved normally and there was no evidence of either excessive polarization or intermittent internal shorts at either electrode.

At the time the decreasing battery voltage reached 24V (about 4 h), only two of the modules (1 and 20) were below the 1.1V level but both of these modules were in voltage reversal, i.e. contributing a negative voltage to the total battery voltage. After a total of 265 minutes, the battery

TABLE IV

Cell Module Voltages During Discharge of Battery No. 34

Cell No.	Cell Voltage 1	2	3	4	5	6	7	8	9	10	11	12
Time Min.												
OCV	1.36	1.38	1.38	1.37	1.38	1.38	1.38	1.34	1.38	1.38	1.39	1.37
1	1.22	1.27	1.25	1.26	1.26	1.26	1.25	1.25	1.25	1.25	1.24	1.20
10	1.23	1.27	1.25	1.25	1.26	1.26	1.25	1.25	1.25	1.25	1.24	1.20
60	1.21	1.25	1.25	1.25	1.26	1.25	1.25	1.24	1.25	1.25	1.24	1.20
120	1.20	1.24	1.25	1.25	1.26	1.25	1.24	1.23	1.24	1.24	1.24	1.19
145	1.20	1.24	1.25	1.25	1.25	1.25	1.24	1.23	1.24	1.24	1.24	1.19
				air circulation fan turned off								
150	1.13	1.20	1.24	1.23	1.24	1.22	1.21	1.21	1.22	1.22	1.22	1.13
166	1.19	1.20	1.24	1.24	1.24	1.23	1.22	1.22	1.23	1.23	1.23	1.14
				air circulation fan turned on								
170	1.19	1.24	1.25	1.25	1.26	1.25	1.25	1.24	1.25	1.25	1.24	1.19
210	1.10	1.24	1.25	1.25	1.26	1.25	1.25	1.24	1.24	1.25	1.24	1.17
240	-0.93	1.24	1.25	1.26	1.26	1.26	1.25	1.24	1.25	1.25	1.24	1.14
265	-0.93	1.25	1.26	1.26	1.26	1.26	1.25	1.24	1.25	1.25	1.24	-1.05
300	-0.93	1.25	1.26	1.26	1.27	1.26	1.26	1.25	1.25	1.26	1.23	-1.18
360	-0.93	1.24	1.26	1.27	1.27	1.26	1.26	1.24	1.25	1.26	1.14	-3.59
420	-0.90	1.25	1.26	1.28	1.28	1.28	1.27	1.26	1.25	1.28	-0.88	-5.39

Cell No.	Cell Voltage 13	14	15	16	17	18	19	20	21	22	Battery Voltage
Time Min.											
OCV	1.38	1.38	1.37	1.37	1.35	1.38	1.38	1.38	1.38	1.39	30.1
1	1.26	1.26	1.26	1.26	1.25	1.26	1.27	1.22	1.20	1.25	26.8
10	1.26	1.26	1.26	1.25	1.25	1.26	1.26	1.22	1.21	1.25	26.9
60	1.25	1.25	1.25	1.25	1.23	1.25	1.25	1.24	1.21	1.25	26.8
120	1.25	1.25	1.25	1.24	1.22	1.25	1.24	1.22	1.20	1.24	26.7
145	1.25	1.25	1.25	1.24	1.22	1.25	1.24	1.17	1.19	1.24	26.6
				air circulation fan turned off							
150	1.22	1.23	1.23	1.21	1.14	1.21	1.23	1.12	1.16	1.24	25.9
166	1.23	1.24	1.23	1.21	1.17	1.22	1.23	1.10	1.14	1.24	26.0
				air circulation fan turned on							
170	1.25	1.26	1.25	1.24	1.23	1.25	1.25	1.14	1.17	1.24	25.6
210	1.25	1.25	1.25	1.24	1.22	1.23	1.24	0.02	1.09	1.24	25.3
240	1.26	1.26	1.25	1.24	1.22	1.24	1.23	0.00	1.06	1.24	22.5
265	1.26	1.26	1.25	1.24	1.21	1.24	1.24	-0.91	0.89	1.24	20.0
300	1.27	1.27	1.25	1.24	1.18	1.24	1.24	-0.93	-1.12	1.24	18.0
360	1.27	1.27	1.25	1.23	1.06	1.22	1.21	-1.02	-1.12	1.23	15.3
420	1.29	1.29	1.25	1.21	-0.81	1.11	1.11	-0.98	-1.13	1.24	9.6

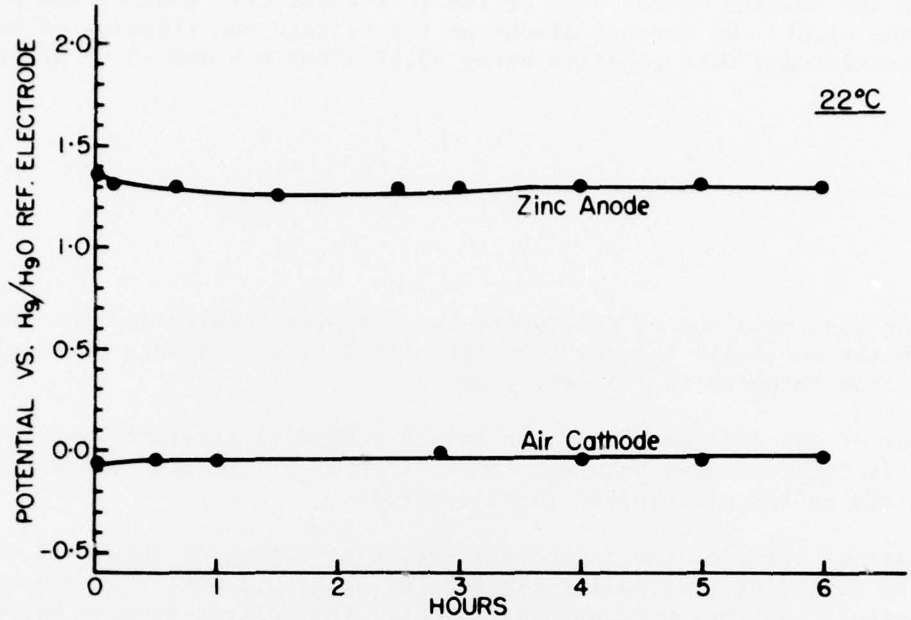

Fig. 20: Electrode Potentials of Cell Module 13, Battery No. 34.

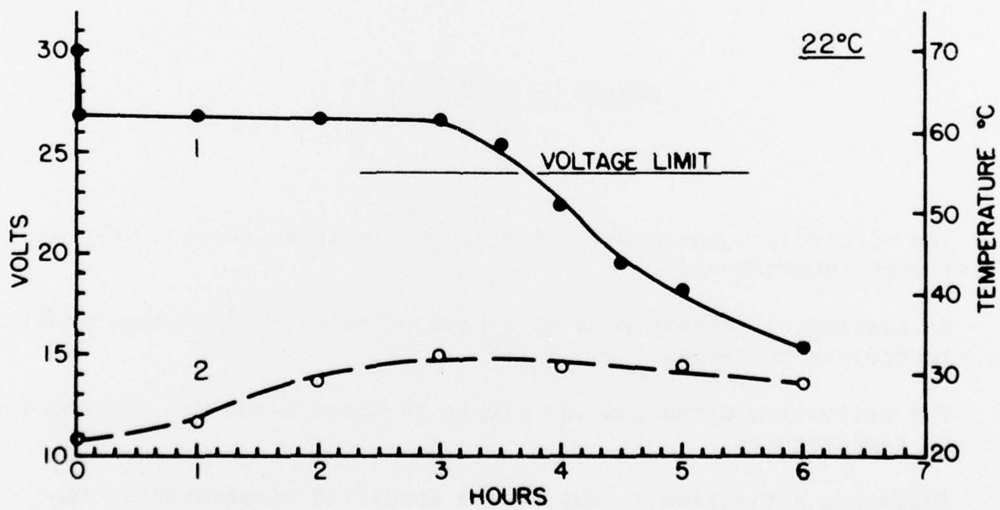

Fig. 21: Discharge at Room Temperature With Forced Air Circulation of Battery No. 34.

1. Voltage 2. Temperature

voltage reached 20V and two more modules (12 and 21) were in voltage reversal. At that time the voltage across each of the four spent cell modules was between -0.9 and -1.0V. On further discharge the voltage contribution of module 12 became increasingly more negative being -3.6V after 6 h and -5.4V after 7 h.

COMMENTS

1. The fact that only one of the twenty-two resealed modules did not leak demonstrates the necessity for new techniques in battery sealing, particularly in cementing the cathodes to the cell frame.

2. All four of the cell modules which failed leaked electrolyte from both bicells and failure may have been due to passivation of the zinc anodes on exposure to air as the electrolyte level dropped.

3. With each of three of the failed modules, the voltage of about -1V could be attributed to an internal cell resistance of about 0.3 ohm. The behaviour of cell module 12 was, however, much different. The voltage dropped below 1.2V only 30 minutes after the start of the discharge, and after failure, the negative voltage contribution to the battery voltage was greater than 5V. These results might be due to high current breakdown of the electrolyte.

SUMMARY OF RESULTS

1. The electrolyte container was prone to leakage, particularly at elevated storage temperatures.

2. No meaningful storage data was obtained because of leakage problems with the electrolyte container.

3. The activation mechanism was simple to operate and met the requirements at all temperatures.

4. Following activation at any of the specified temperatures, the battery voltage attained a level greater than 20V in less than 1 min and did not drop below 20V upon application of the 8 ohm load.

5. Leakage of electrolyte during activation and discharge was a serious problem.

6. Disintegration of the separator led to internal anode to cathode shorts, decreased battery capacity and promoted rapid self-discharge on activated stand.

7. Convective air flow through the cell stack was not sufficient to supply the oxygen required by the air cathodes.

8. When discharged with forced air circulation, batteries gave four hours of operation within the voltage and current specifications at all temperatures investigated from -40° to 49°C. No sample gave the five hours required at 22°C.

CONCLUSIONS

Despite the design faults uncovered during the evaluation, the battery was shown to be capable of delivering the required power for four hours at -40°. This is twice as long as called for by the contract specification and much longer than anticipated. Only at 22°C did the battery fail the electrical requirements and there is every indication that the use of proper separators and sealants would extend the battery capacity to meet the specification. The problems of electrolyte storage, sealing of cell stack components and separator deterioration should be readily solved with available materials and techniques. There is some doubt, however, about the possibility of obtaining sufficient convective air flow through a cell stack composed of 44 bicells while remaining within the specified overall maximum battery length of 12.2 in.

After discussions with the contractor the following improvements in design were suggested for inclusion in any batteries which might be built in the future.

1. The electrolyte should be housed in a molded plastic upper battery compartment rather than a plastic bag. An open slot along the bottom of the compartment would be covered with a strip of plastic known to be unreactive with aqueous potassium hydroxide over a wide range of temperatures. PTFE is a possible candidate material.

2. Cathodes should be built into the cell frame during the injection molding of the cell frame. This technique has been used by the contractor to eliminate electrolyte leaks at the cathode-cell frame joint in button-size zinc/air batteries.

3. The cathode box should be re-designed to permit testing for leaks prior to the insertion of the zinc anode.

4. A separator capable of rapid wetting at -40° but unreactive with electrolyte at temperatures as high as 70°C should be used. Such a material has recently been developed at DREO (3).

5. Spacer ribs rather than plastic screen should be used to maintain a fixed distance between bicells. The ribs should be angled to promote convective air circulation and the inter-cell spacing should not be less than 1/16 in.

6. Each bicell should be affixed both to the activation tray and the lower battery compartment to provide better protection from shock and vibration.

ACKNOWLEDGEMENT

The authors wish to acknowledge the valuable technical assistance provided by Mr. G.E. Patton.

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APPENDIX A

EVALUATION PLAN FOR ZINC/AIR BATTERIES FOR AN/TRN-30

I. PHYSICAL INSPECTION

(a) Visually examine for physical damage.

(b) Visually examine for electrolyte leakage.

(c) Record linear dimensions and weight.

All batteries to be subjected to these tests upon arrival.

II. UNACTIVATED STORAGE

Unless otherwise stated, batteries will be stored in an upright position in a refrigerated room with the temperature maintained at 0°C.

(a) Three batteries will be stored for 90 days at 32°C and 90% relative humidity. Two of these will be stored upright and the other upside down (electrolyte case down). One of the upright batteries and the battery stored upside down will be subjected to Electrical Discharge Test V(a). The remaining battery will be subjected to Electrical Discharge Test V(c).

(b) One battery will be stored upright at 71°C for 30 days. Following storage it will be subjected to Electrical Discharge Test V(b).

(c) Two batteries will be placed upright in an environmental chamber and subjected to 10 complete temperature cycles, each cycle consisting of 8 hours at 49°C followed by 8 hours at -29°C. Following this one battery will be subjected to Electrical Discharge Test V(a) and the other to V(c).

(d) Two batteries will be placed upright in an environmental chamber at -18°C and the pressure shall be reduced to a value corresponding to an altitude of 50,000 ft. After 6 hours, the batteries shall be removed. One will be subjected to Electrical Discharge Test V(c) and the other to V(d).

(e) Twelve batteries will be stored at room temperature. A lot of three batteries shall be removed and discharged after 3 months, 6 months, 9 months, and 12 months. One of each lot shall be subjected to Electrical Discharge Test V(a), the second to V(b) and the third to V(c).

III. ACTIVATED STORAGE

Two batteries, having been maintained at -40°C for at least 12 hours will be activated and left in an environment of -40°. After 4 hours, one battery will be subjected to Electrical Discharge Test V(a). After 24 hours the second battery will be subjected to Electrical Discharge Test V(a).

The activated storage tests will also be carried out with batteries maintained at 22°C and subjected to Electrical Discharge Test V(b) and to batteries maintained at 49°C and subjected to Electrical Discharge Test V(d).

IV. DISCHARGED STORAGE

All discharged batteries shall be stored at room temperature and subjected to Physical Inspection Tests I(a) to I(d) 24 hours after discharge, one week after discharge and two weeks after discharge.

V. CONTINUOUS ELECTRICAL DISCHARGE TESTS

Batteries will be situated upright in an environmental chamber capable of controlling and maintaining the interior temperature within ±0.5°C over the temperature range of interest. Batteries will be equilibrated at the desired temperature for discharge for at least 12 hours prior to discharge. Provision shall be made for the admission of air to the chamber. Such air shall be at the same temperature as that of the chamber and this shall be accomplished by passing the air through a copper coil immersed in a bath maintained at the same temperature as the chamber. A baffle shall prevent the admitted air from coming directly in contact with the battery. The batteries will be activated in the chamber if the chamber volume permits this. If not, the batteries will be removed, activated and returned to the chamber in the shortest possible time. When the Open Circuit Voltage of an activated battery has reached 24V, the battery will be discharged through a fixed resistance of 8.0 ± 0.1 ohm which shall be situated outside of the environmental chamber. A record shall be kept of the time required to operate the activation mechanism, the time elapsed between operation of the activation mechanism and the attainment of a battery OCV of 24V as well as the time

elapsed from the initiation of the discharge until the battery has come up to 20V. During the discharge, current, battery voltage and electrolyte temperature will be recorded with time. The discharge will be stopped when the battery voltage falls below 20V.

At least three batteries will be discharged at each of the temperatures described in Tests V(a) to V(d).

V(a) The battery shall be discharged at -40°C.

V(b) The battery shall be discharged at -29°C.

V(c) The battery shall be discharged at 22°C.

V(d) The battery shall be discharged at 49°C.

APPENDIX B

REVISED EVALUATION PLAN

I. PHYSICAL INSPECTION

(a) Visually examine for physical damage.

(b) Visually examine for electrolyte leakage.

(c) Record linear dimensions and weight.

II. EFFECT OF AIR CIRCULATION ON DISCHARGE TIME

Discharge:

(a) Four batteries as described in Test III(c) but with batteries located on a laboratory bench.

(b) One battery as described in Test III(c) with battery located on a laboratory bench and the side panels of the lower battery compartment removed to allow unimpeded convective air flow through the cell stack.

(c) One battery as described in Test III(c) but with chamber door open and forced air circulation by the chamber fan to be initiated upon attainment of a battery voltage of 24V. The discharge with forced circulation will be continued until the battery voltage again decreases to 20V.

(d) One battery as described in Test III(c) but with chamber door open and circulation fan on.

III. CONTINUOUS ELECTRICAL DISCHARGE TESTS

Batteries will be situated upright in an environmental chamber capable of controlling and maintaining the interior temperature within ± 0.5°C over the temperature range of interest. Batteries will be equilibrated at the desired temperature for discharge for at least 12 h prior to discharge. Provision shall be made for the admission of air to the chamber. Such air shall be at the same temperature as that of the chamber and this shall be accomplished by passing the air through a copper coil immersed in a bath maintained at the same temperature as the chamber. A baffle shall prevent the admitted air from coming directly in contact with the battery. The batteries will be activated in the chamber if the chamber volume permits this. If not, the batteries will be removed, activated and returned to the chamber in the shortest possible time. When the Open Circuit Voltage of an activated battery has reached 24V, the battery will be discharged through a fixed resistance of 8.0 ± 0.1 ohm which shall be situated outside of the environmental chamber. A record shall be kept of the time required to operate the activation mechanism, the time elapsed between operation of the activation mechanism and attainment of a battery OCV of 24V as well as the time elapsed from the initiation of the discharge until the battery has come up to 20V. During the discharge, battery voltage and electrolyte temperature will be recorded with time. The battery current can be calculated by dividing the battery voltage by the load resistance (8.0 ohm). The discharge will be stopped when the battery voltage falls below 20V.

At least two batteries will be discharged at each of the temperatures given below.

(a) The battery shall be discharged at -40°C.

(b) The battery shall be discharged at -29°C.

(c) The battery shall be discharged at 22°C.

(d) The battery shall be discharged at 49°C.

IV UNACTIVATED STORAGE

Unless otherwise stated, batteries will be stored in an upright position in a refrigerated room with the temperature maintained at 3°C.

(a) Three batteries will be stored for 90 days at 32°C and 90% relative humidity. Two of these will be stored upright and the other upside down (the electrolyte container on the bottom). One of the upright batteries and the battery stored upside down will be subjected to Electrical Discharge Test

III(a). The remaining battery will be subjected to Electrical Discharge Test III(c).

(b) One battery will be stored upright at 71°C for 30 days. Following storage it will be subjected to Electrical Discharge Test III(b).

(c) Eight batteries will be stored at room temperature. A lot of two batteries shall be removed and discharged after 90 days, 180 days, 270 days and 360 days. One of each lot shall be subjected to Electrical Discharge Test III(a) and the second to III(c).

V. ACTIVATED STORAGE

Two batteries, having been maintained at 22°C for at least 12 hours, will be activated and continue to be maintained at 22°. After 4 hours, one will be subjected to Electrical Discharge Test III(c). After 24 hours the second battery will be subjected to Electrical Discharge Test III(c).

VI. DISCHARGED STORAGE

All discharged batteries shall be stored at room temperature and subjected to Physical Inspection Tests I(a) and I(b) 24 h after discharge and two weeks after discharge.

VII. EFFECT OF INDIVIDUAL CELL MODULE PERFORMANCE ON BATTERY PERFORMANCE

Remove the upper battery compartment and electrolyte bag from a battery. Connect lead wires so that the voltage of each of the 22 cell modules can be recorded. Introduce a mercury/mercuric oxide reference electrode into one cell module so that both cathode and anode potentials of that cell are recorded.

Activate the battery at room temperature with 1350 ml of 33% KOH electrolyte also at room temperature and discharge the battery into the 8 ohm load. Provide adequate air circulation through the cell stack during the discharge by means of a fan.

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13. ABSTRACT

Despite problems with leakage of electrolyte, disintegration of the separator material and air starvation at the cathodes, batteries gave four hours of discharge at 3A, while maintaining the battery voltage between 20-30V at temperatures between -40° and 49°C. Suggestions were made for improvements in the battery design.

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